THE STRUCTURES AND PROPERTIES OF THE POLYPHOSPHATES

BY

ORVILLE FARROW HILL

B. S., James Millikin University, 1940

M. S., University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

THE STRUCTURES AND PROPERTIES OF THE POLYPHOSPHATES

Introduction

Compounds of pentavalent phosphorus, in particular the polyphosphoric acids and their salts, have attained an important position as industrial chemical commodities. While research has greatly expanded our knowledge of phosphorus chemistry, the relationships existing among the various polyphosphates and metaphosphates has not been well-defined. The present investigation was undertaken in order to bring about some clarification of our foundamental knowledge in this chaotic field.

Hydration of Phosphorus (V) Oxide

The development of an analytical procedure for the determination of triphosphoric acid[1] enabled Bell[2] to determine the equilibrium compositions of the "strong liquid phosphoric acids" containing 72.4-88.8% P_4O_{10}. He has shown that these acids are mixtures of ortho-, poly-, and metaphosphoric acids rather than well-defined chemical individuals. Using the model of the P_4O_{10} molecule[3], known to exist both in the vapor and in the α form of the solid, the author has studied the hydration of phosphorus (V) oxide by a theoretical approach which involves a statistical consideration of the stepwise addition of water. This theoretical study has shown that the "strong liquid phosphoric acids" must be mixtures and that it is impossible to obtain a single chemical species of high P_4O_{10} content by the addition of water to phosphorus (V) oxide. Furthermore, this approach has made it possible to show what poly- and metaphosphoric acids may exist and what their structures must be. For instance, tri- and tetrametaphosphoric acids must possess cyclic structures consisting of six and eight membered rings, respectively.

Discrepancies exist between Bell's observed compositions and those calculated theoretically on the basis of such a statistical treatment. These differences may be due to any one or several of the following factors: (a) the uncertainty of the assumptions involved in the statistical treatment, i. e., that all P-O-P bonds are equal and undergo rupture statistically and that all hypothetical intermediate acids are stable, (b) the question of existence of branched chain structures among the polyphosphoric acids, (c) the possibility of disproportionation among the polyphosphoric acids, and (d) the effect of temperature upon the stability of the polyphosphoric acids.

Extension of this approach to other solvolytic reactions involving phosphorus (V) oxide has proven quite useful. Products containing a high P_4O_{10} content prepared by the action of a solvent on P_4O_{10} must consist of mixtures and cannot be well-defined individual chemical compounds. For example, the German insecticide, hexaethyl tetraphosphate, HETP, is a mixture. It has recently been shown that the active ingredient is tetraethyl pyrophosphate[4]. Consequently, the most effective agent would be that composition which contains tetraethyl pyrophosphate in largest amounts and does not necessarily result when synthesis is effected from components in ratios corresponding to those required empirically for pure TEPP.

Acid-Base Character of the Polyphosphates

According to the Lewis concept of acids and bases, "an acid is capable of accepting a share in a lone electron pair from a base to form a coordinate covalent bond. A base donates a share in a lone electron pair to the acid"[5]. Consequently, by taking into consideration the structures of the polyphosphates, it becomes obvious that a series of compounds of increasing acidity are obtained as polymerization and/or anionic aggregation take place among the phosphates. Thus, the coordinatively saturated orthophosphate ion, PO_4^{-3}, be-

haves as a base while the pyrophosphate ion, $P_2O_7^{-4}$, is less basic; the metaphosphate, $(PO_3)_x^{-x}$, is more acidic while phosphorus (V) oxide is the most acidic of the phosphorus-oxygen compounds. Therefore, it should be possible to bring about interconversion among the poly- and metaphosphates by the employment of the appropriate high temperature acid or base. This change in aggregation of the anionic acid or base is analogous to that occurring with a change in the pH of aqueous solutions of chromates, tungstates, molybdates and vanadates.

The preparation of the polyphosphates by heating mono- and/or dihydrogen orthophosphates may be looked upon as a well-known example of this phenomenon, the hydrogen ion being the acid which brings about an increase in the state of aggregation of the phosphate. A sodium metaphosphate has been prepared by heating a mixture of five parts of Na_2HPO_4, one part of NH_4NO_3 and one part of NH_4Cl[6]. The author has shown that potassium dichromate and potassium hydrogen sulfate will react with sodium orthophosphate at higher temperatures to give pyrophosphate. Insoluble sodium metaphosphate is formed when sodium pyrophosphate is heated with ammonium chloride at 300°C. The presence of the insoluble sodium metaphosphate was verified by x-ray powder diffraction patterns.

A well-known case of degradation of polyphosphate by high temperature bases is the metaphosphate bead test, formerly used widely in qualitative analyses. Sodium polymetaphosphate is depolymerized by metallic oxides at high temperatures to give pyro- and/or orthophosphates[7]. Fusion of a mixture of sodium sulfide and sodium polymetaphosphate yields sodium monothiophosphate[8]. The author has shown that fusion of sodium polymetaphosphate with either sodium hydroxide or sodium carbonate gives sodium orthophosphate as the completely neutralized product. Fusion of a mixture of sodium polymetaphosphate with sodium fluoride yields sodium monofluophosphate. When sodium chloride is used

instead of sodium fluoride, sodium pyrophosphate is the product of the reaction. Since sodium monofluophosphate is known to be thermally unstable to decompose to give sodium pyrophosphate, it is proposed that degradation of polymetaphosphate to pyrophosphate by chloride takes place through the formation of an intermediate, unstable monochlorophosphate. The latter has not been isolated experimentally.

It is suggested that this acid-base concept of the relationship of the poly- and metaphosphates may be extended to other polyanionic systems.

Preparation of Monofluophosphates by Polyphosphate-Fluoride Fusions

With the formulation of the acid-base concept presented above, it becomes evident that monofluophosphates should be formed by polyphosphate-fluoride fusion reactions. Monofluophosphates were previously prepared by heating ammonium fluoride with phosphorus (V) oxide[9]. More recently, preparation of monofluophosphates has been accomplished by neutralization of the free acid which may be obtained by the action of anhydrous hydrogen fluoride on "metaphosphoric acid." Pure products in high yields are difficult to prepare by either reaction. Fluosulfates[10] and monothiophosphates[8] had already been prepared by fusion reactions of the kind proposed here for the preparation of monofluophosphates.

Mixtures of sodium poly- and/or polymetaphosphates with sodium fluoride were fused in a platinum dish in an ordinary muffle furnace at certain temperatures for given periods of time. The fusion melts were cooled and analyzed for the various phosphates[1], fluoride[11,12] and monofluophosphate. The latter was determined qualitatively by Lange's method[9], involving the preparation of the characteristic silver salt, and quantitatively by the precipitation of the barium salt.

It was shown that sodium monofluophosphate may be prepared in excellent yield by heating a mixture of sodium

polymetaphosphate and sodium fluoride in a 1:1 mole ratio at 700°-800°C., just long enough to bring about complete fusion, in accordance with the empirical equation:

$$NaPO_3 + NaF \rightarrow Na_2PO_3F$$

The product thus obtained is contaminated with pyrophosphate. It may be purified by removal of the impurity with silver monofluophosphate, removal of the excess silver ion by sodium hydroxide, and crystallization by alcoholic extraction of the water from the solution. Sodium monofluophosphate is also a product in the fusion reaction involving sodium triphosphate and sodium fluoride. When mixtures of sodium pyrophosphate and sodium fluoride were fused, no monofluophosphate was found among the products.

If sodium monofluophosphate (or a mixture of a sodium polyphosphate and sodium fluoride) is heated for a prolonged period, no monofluophosphate is found in the residue. The decomposition of the monofluophosphate takes place in a wet atmosphere to give hydrogen fluoride in accordance with the following equations:

$$PO_3F^{=} + H_2O \rightarrow HPO_4^{=} + HF$$
$$2HPO_4^{=} \rightarrow P_2O_7^{-4} + H_2O$$

When sodium monofluophosphate is heated in a dry atmosphere, phosphorus (V) oxyfluoride, POF_3, is probably the volatile product.

Monofluophosphates of metals whose sulfates are insoluble or sparingly soluble may be prepared easily from the sodium polymetaphosphate-sodium fluoride fusion residue. Ag_2PO_3F and $BaPO_3F \cdot H_2O$ were prepared in good yields by this method.

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VITA

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He entered the graduate school of the University of Illinois in June, 1940, and received the degree of Master of Science in chemistry in June, 1941. He served as Assistant in Chemistry in the Inorganic Division from September, 1940, to June, 1942. From that time until September, 1946, he served as a research chemist on the Plutonium Project. In 1946 he was awarded the Victor Chemical Company Fellowship and returned to the University of Illinois to complete his doctorate studies.

The author is a member of the American Chemical Society, Sigma Xi, and Alpha Chi Sigma.

He is a joint author of the following papers:

1) Audrieth, L. F., Scott, L. D., and Hill, O. F., J. Am. Chem. Soc., **64,** 2498 (1942).
2) Audrieth, L. F., and Hill, O. F., "Recent Developments in the Chemistry of Phosphorus," presented at the 112th meeting of the American Chemical Society, New York City, September, 1947; to be published in the J. Chem. Ed.
3) Audrieth, L. F., and Hill, O. F., "The Structure of the Polyphosphoric Acids," presented at the A. A. A. S. meeting in Chicago, Illinois, December, 26, 1947.